

Comparison of Density Functional Theory Models' Ability to Reproduce Experimental ^{13}C -NMR Shielding Values

KENNETH B. WIBERG

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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ABSTRACT: The ability of several density functionals to reproduce experimental ^{13}C -NMR shielding was examined, and it was found that the MPW1PW91 hybrid functional with the 6-311 + G(2d,p) basis set gave generally good agreement with the observed isotropic shielding values. The MP2/GIAO procedure was not as successful, leading to significant underestimation of the paramagnetic terms in most cases. All of the models reproduced the trends in the tensor components of the chemical shift. MPW1PW91 gave smaller errors with the saturated groups, and the two models were comparable for the other groups that were studied. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 1299–1303, 1999

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Introduction

The *ab initio* calculation of NMR chemical shifts serves several useful purposes: it helps to determine the structures of molecules in solutions,¹ it provides a test of theoretical models via a comparison with the experimental data, and the results

may be interpreted in such a way that the origin of the differences in chemical shifts may be examined.² In these calculations, the GIAO method^{3,4} is the more widely used. The results obtained using the Hartree–Fock (HF), MP2, and density functional theory (DFT) theoretical models for a number of small molecules for which the isotropic shifts and the tensor components are both available are compared in order to see which approach is the more satisfactory.

The density functional approach, such as B3LYP, has some advantages over MP2 for NMR shielding

Correspondence to: K. B. Wiberg; e-mail: kenneth.wiberg@yale.edu

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calculations. First, the execution times and demand for disk storage are both much smaller for the DFT methods than for MP2. Second, the DFT methods lead to a simple $n/2 \times n/2$ density matrix (where n = the number of electrons) that can be converted into "orbitals" that are doubly occupied. This provides a much more convenient framework for the analysis of chemical shifts⁵ than MP2 where there are both $n/2$ largely occupied orbitals and many slightly filled orbitals.

There are many DFT models, and although it is widely used, B3LYP may not prove to be the more satisfactory for GIAO NMR calculations. All of the methods correctly reproduce the diamagnetic part of the shielding that depends only on the ground state electron density distribution. This can be seen in the long axis shielding component for acetylene that has only diamagnetic shielding because of the symmetry. Here, using the 6-311 + G(2d,p) basis set, all of the methods give 279 ppm, which is in good agreement with the experimental value of 276 ppm.⁶

The differences in calculated values for a given compound then arise from the paramagnetic terms that depend on both the ground state orbitals and the virtual orbitals. It is likely that some DFT methods give a more satisfactory representation of the virtual orbitals than B3LYP. This was found to be the case in calculations of the electronic transi-

tions for some carbonyl compounds.⁷ The present investigation is concerned with a comparison of the ability of different DFT methods to reproduce experimental NMR shielding values for some small organic molecules for which the isotropic shielding and its tensor components are both known experimentally.⁴ For a comparison, the HF/GIAO and MP2/GIAO⁸ calculated shielding were also obtained.

Isotropic Magnetic Shielding

The quantity that is calculated is the shielding of a carbon nucleus by the electrons in the molecule. The shielding (σ) is related to the chemical shift (δ) by

$$\sigma = 186.4 - \delta,$$

where 186.4 is the shielding of tetramethylsilane (TMS).⁹ It should be noted that the shielding and chemical shift scales go in opposite directions. The experimental chemical shifts were converted to shielding using the above expression.

The following hybrid functionals were employed: B3LYP, B1LYP, B3PW91, B3P86, and MPW1PW91. The B3 terms make use of the Becke three parameter functional,¹⁰ the B1 term makes use of the Becke one parameter functional,¹¹ and

TABLE I.
Calculated and Observed Nuclear Shielding.

Compound	Atom	HF	B3LYP	B1LYP	B3PW91	B2P86	MPW	MP2	Expt
Methane	C	195	190	190	192	192	193	201	195
Tetramethylsilane	CH ₃	193	183	184	186	186	187	197	186
Ethane	CH ₃	180	174	175	177	178	178	188	177
Propane	CH ₃	174	165	165	168	168	169	177	170
Methanol	CH ₃	145	130	131	134	134	135	144	136
Ethanol	CH ₃	175	165	165	168	169	169	179	167
Acetaldehyde	CH ₃	162	149	150	152	152	153	163	155
Acetone	CH ₃	164	152	152	155	154	156	165	155
Cyclobutane	CH ₂	169	155	156	159	159	161	170	161
Bicyclobutane	CH ₂	163	149	150	152	152	153	163	154
Bicyclobutane	CH	162	186	187	188	189	190	202	192
Ethanol	CH ₂	137	120	121	124	124	126	135	132
Ethene	CH ₂	62	52	53	55	55	56	74	60
Propene	CH ₂	71	62	63	64	64	65	81	73
Propene	CH	48	38	38	42	42	43	61	53
Acetylene	CH	117	110	111	112	112	112	126	116
Acetaldehyde	C=O	-12	-24	-23	-21	-21	-20	5	-14
Acetone	C=O	-20	-31	-31	-27	-27	-26	-24	-22
RMS error		9	7	7	5	5	4	10	

RMS, root mean square.

MPW1 is the Barone–Adamo one parameter functional.¹² LYP refers to the Lee–Yang–Parr correlation functional,¹³ P86 is that developed by Perdew,¹⁴ and PW91 is the Perdew–Wang gradient corrected correlation functional.¹⁵

The calculated shielding values obtained using the 6-311+G(2d,p) basis set are compared with the experimental isotropic shieldings in Table I. This basis set was found to be generally satisfactory for NMR shielding calculations.⁴ The root mean square errors with respect to the experimental values are given as the last row of the table. It can be seen that the MPW1PW91 is the most satisfactory of the DFT functionals. With the saturated carbons, the deviation from the experiment is remarkably small.

It may be noted that the DFT methods are generally more satisfactory than MP2 in reproducing the experimental values. With respect to HF/GIAO, the DFT methods give somewhat smaller shielding values (corresponding to larger paramagnetic terms) whereas MP2 gives significantly larger calculated shielding in most cases (corresponding to smaller paramagnetic terms). The deficiency with MP2/GIAO is frequently minimized by converting the shielding to chemical shifts with respect to TMS. It should be noted that the MP2 calculation gives the shielding of TMS as 197 ppm, which is considerably larger than the experimental value of 186 ppm. The B3LYP calculated shielding for TMS is 183 ppm.

The relationship between the calculated and experimental isotropic shielding is examined in Figure 1. MPW1PW91 and MP2 both give a fairly good correlation, but in each case the slope is not unity and the intercept is not zero. The main problem is found with the strongly deshielded carbonyl groups. The two theoretical models give calculated shieldings that are very well correlated (Fig. 1c), and here the carbonyl groups fall closer to the line. Again, the slope is not unity and the intercept is not zero. It will be interesting to see if this relationship holds for a larger range of com-

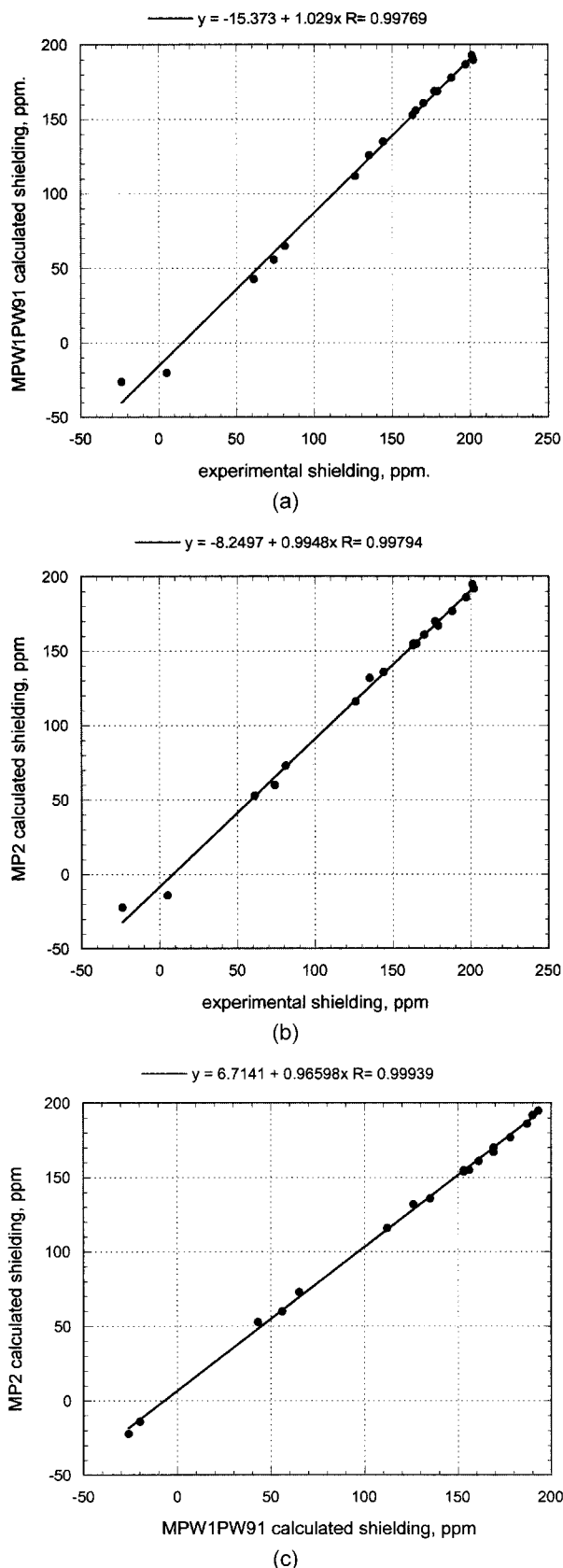


FIGURE 1. The relationship between (a) the MPW1PW91 calculated isotropic shielding and the experimental values, (b) the MP2 calculated isotropic shielding and the experimental values, and (c) the MP2 and MPW1PW91 calculated isotropic shieldings.

pounds, allowing the MP2 shielding to be estimated from the DFT values.

Tensor Components of Magnetic Shielding

A detailed examination of the tensor components of the magnetic shielding is made more difficult by the larger experimental uncertainties associated with these quantities (generally 2–5 ppm). The results of the calculations for the methyl groups are summarized in Figure 2. All of the calculations reproduce the trends in the tensor components quite well. In most cases the MPW1PW1 model reproduces the experimental values better than MP2. Among the DFT methods, the trends toward greater shielding when going from model 1 to 5 continues.

A similar comparison for methylene groups is shown in Figure 3. Again, all of the methods reproduce the general trends in the shielding. In some cases, MPW1PW91 is significantly more satisfactory than MP2, but the reverse is also found. A comparison for some CH groups and carbonyl groups is shown in Figure 4. The trends are reproduced, but neither MPW1PW91 nor MP2 is clearly the more satisfactory.

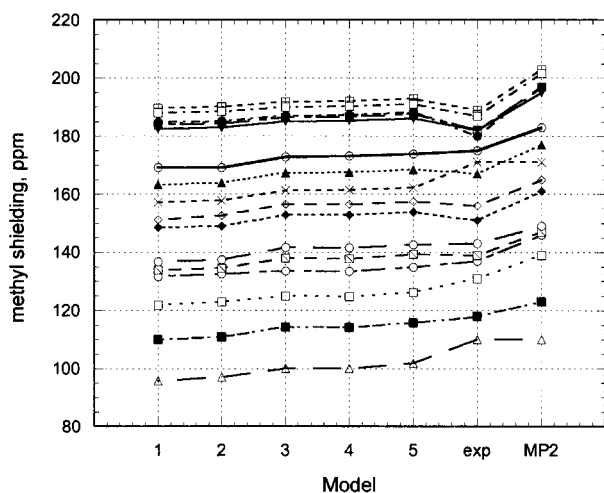


FIGURE 2. The relationship between the calculated and observed tensor components of the shielding for some methyl groups. The groups are (from top to bottom) acetone σ_{33} , acetaldehyde σ_{33} ; ethane σ_{33} , propane σ_{33} , methanol σ_{33} ; ethanol σ_{33} ; ethane σ_{11} ; ethanol σ_{22} ; propane σ_{22} ; propane σ_{11} ; ethanol σ_{11} ; acetone σ_{22} ; acetone σ_{11} ; acetaldehyde σ_{22} ; acetaldehyde σ_{11} ; methanol σ_{22} ; and methanol σ_{11} .

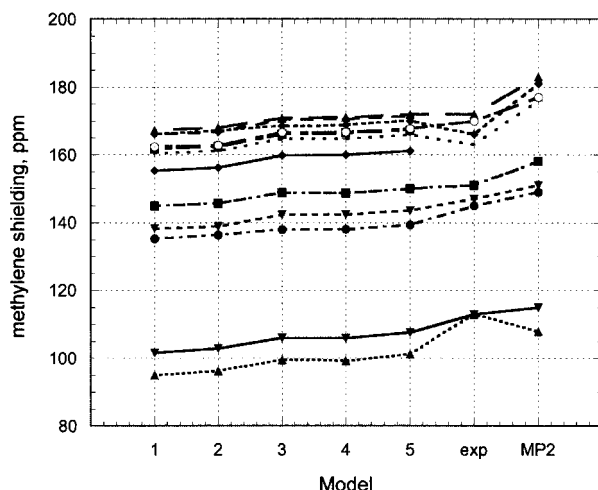


FIGURE 3. The relationship between the calculated and observed tensor components of the shielding for some methylene groups. The groups are (from top to bottom) cyclobutane σ_{33} , bicyclobutane σ_{33} ; propane σ_{33} ; ethane σ_{33} , cyclobutane σ_{22} ; propane σ_{22} ; propane σ_{11} ; bicyclobutane σ_{22} ; cyclobutane σ_{11} ; bicyclobutane σ_{11} ; ethanol σ_{22} ; and ethanol σ_{11} .

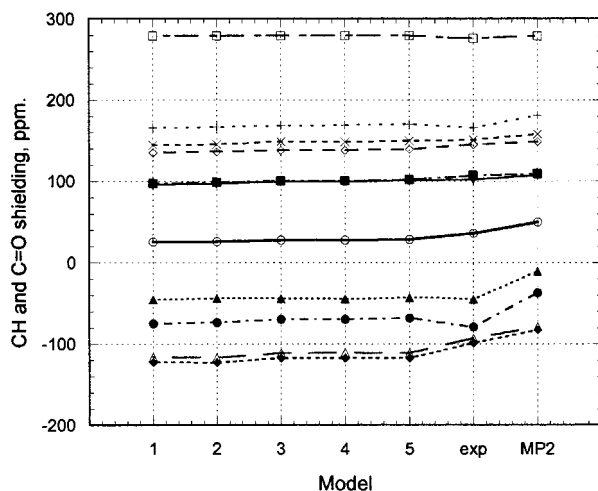


FIGURE 4. The relationship between the calculated and observed tensor components of the shielding for some CH and C=O groups. The groups are (from top to bottom) acetylene; parallel; bicyclobutane σ_{33} , σ_{22} ; bicyclobutane σ_{11} ; acetone σ_{11} ; acetaldehyde σ_{33} ; acetylene perpendicular; acetaldehyde σ_{22} ; acetone σ_{22} ; and acetone σ_{11} , acetaldehyde σ_{11} .

Conclusions

The MPW1PW91 hybrid density functional generally gives calculated isotropic shielding values that are in very good agreement with the

observed values. MP2 was found to be less satisfactory and to underestimate the paramagnetic terms for saturated groups. The density functional methods have two advantages over MP2: they require much fewer computational resources for a given molecule, and the density matrices that result from these calculations are more easily studied in examining the origin of the differences in chemical shifts.²

Calculations

All of the calculations were carried out using Gaussian 98¹⁶ and MP2/6-311 + G** optimized geometries.

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